

Performance of Direct Methanol Fuel Cells with Sputter-Deposited Anode Catalyst Layers

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Performance of direct methanol fuel cells with sputter-deposited Pt-Ru anodes was investigated. The thin film catalyst layers were characterized using X-ray diffraction, energy dispersive X-ray analysis, Rutherford backscattering spectroscopy, and X-ray photoelectron spectroscopy. Different catalyst loadings and membrane electrode assembly (MEA) fabrication processes were tested. The maximum power density achieved at 90°C was 100 mW/cm², and almost 75 mW/cm² was attained with a loading of only 0.03 mg/cm². The results demonstrate that a catalyst utilization of at least 2300 mW/mg can be achieved at current densities ranging from 260 to 380 mA/cm². The application of the sputter-deposition method for MEA fabrication is particularly attractive for commercialization of direct methanol fuel cell technology.

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The past 10 years have seen a proliferation in proton exchange membrane (PEM) direct methanol fuel cell (DMFC) research and development.¹⁻⁴ There has been a tenfold increase in the power density output of a DMFC between 1992 and 1996.⁴⁻⁸ Using pressurized air at 90°C, laboratory DMFCs can achieve ~230 mW/cm²,^{5c,d} almost 40% of the power available from a commercially produced H₂-air fuel cell.⁹ (This reduced power density is acceptable because there is no need for a fuel reformer to create H₂, decreasing the system complexity and cost, increasing transient response, etc.⁶) As a result of this and other improvements, several portable applications in the 10-1000 W range have become attractive.^{1-3,5,6} However, a high anode catalyst loading of 2.5-4 mg/cm² is required to attain this power density, giving it a catalyst utilization of, at best, 100 mW/mg of PtRu. At an anode catalyst loading of 4 mg/cm², corresponding to 16 g/kW, the anode catalyst in a DMFC would cost \$154/kW (2000 prices: \$470/oz Pt, \$70/oz Ru¹⁰). Reducing this loading to ~0.4 g/kW would reduce the anode catalyst cost to \$3.85/kW. In the size range appropriate for vehicular fuel cells (~25-50 kW^{9,11}), this constitutes a substantial reduction in total cost.

Conventional methods for applying fuel cell catalysts to form composite anode catalyst layers involve painting, spraying, or printing a porous gel consisting of catalyst particles in a matrix of proton conducting ionomer onto the Nafion 117 membrane and/or carbon electrode.^{5,6,12-15} The proton conducting ionomer (usually Nafion-H) provides an ion-conducting medium to transport protons from the anode catalyst to the cathode. The hydrophilic pores allow CO₂ generated at the anode catalyst to escape. An interconnected network of catalyst particles provides electronic conductivity to the gas-diffusion electrode. There are several aspects of the conventional membrane/catalyst interface structure which contribute to poor catalyst utilization. The ionomer in the catalyst layer impairs the electronic conductivity between catalyst particles and between the electrode and catalyst particles. The Nafion encasement of catalyst particles should induce some mass-transfer related reduction of cell voltage, but this is likely to be very small as Nafion is highly permeable to methanol.⁶ Porosity adds to the thickness of the catalyst layer, increasing the cell's ohmic resistance. A methanol concentration gradient exists within the thickness of the catalyst layer, and as a result successive 'layers' of catalyst are poorly utilized.¹⁶

Few attempts have been made to reduce the amount of Pt-Ru catalyst used in the anode of the DMFC. Arico *et al.* investigated a DMFC with an unsupported anode catalyst loading as low as 2 mg/cm², but achieved a power density at 90°C of only ~170 mW/cm² using 20 psig oxygen.¹⁷ Carbon-supported Pt-Ru catalysts, advantageous for H₂-air fuel cells, do not provide an overall benefit to the

DMFC. It has been shown that although higher catalyst utilization (mW/mg) can be attained in DMFCs with supported PtRu catalysts, only unsupported catalysts will provide the power densities needed in commercial DMFCs.^{8,17} Use of carbon-supported catalyst at 10-20% metal loading and catalyst loading of 1 mg/cm² can lead to thick anode catalyst layers owing to the low density of carbon. The increased ohmic resistance associated with the thick layer of supported catalysts at the anode has a large impact on DMFC performance at high current densities. Thus carbon-supported electrodes pose limitations in DMFCs, and unsupported catalysts have been preferred.

Sputter deposition (SD), a procedure routinely used in manufacturing thin films,¹⁸ has been used to deposit Pt anode- and cathode-catalyst layers in a H₂-air fuel cell.¹⁹⁻²³ In most of these cases, however, SD was used only to enhance catalyst utilization in fuel cells with conventionally applied Pt catalyst.¹⁹⁻²² Cha and Lee have recognized that sputtering is a new method of applying the Pt catalyst and necessitates a new methodology for creating the membrane electrode assembly (MEA) structure.²³ They obtained the highest utilization of Pt catalyst by alternating layers of sputtered Pt (50 Å thick) and a painted mixed electron and proton-conducting layer of carbon black (XC-72) particles in an ink of the Nafion monomer. Repeating successive applications of these layers up to five times continued to improve the E-i characteristics of the cell. Cells made with this process achieved ~90% of the power density available in a conventionally manufactured H₂-air fuel cell with ~10% of the Pt catalyst. However, because this procedure requires the removal of the membrane from the vacuum sputtering chamber, application and drying of the Nafion ink, and reintroduction into vacuum for each set of layers, it is not practical for large scale manufacturing.

This paper describes our attempt to apply the catalyst layers and create the DMFC MEA structure by SD. Although the catalytic activities of some SD catalysts for methanol oxidation have been measured,²⁴ performance of a polymer electrolyte membrane-based DMFC with SD anode catalyst has not been reported until recently.²⁵ SD should be considered not only as a unique way to deposit the catalyst in a PEMFC MEA, but also as a new way to create the liquid/gas diffusion structure in an MEA. SD catalyst materials differ from catalysts deposited in the conventional manner in morphology, surface chemical compositions, phase compositions, and interfaces with the gas (CO₂), liquid (methanol and water), and electrode. It is necessary that the MEA perform the three functions of proton conductivity, electrical conductivity, and fuel accessibility.

This study focuses on film characterization and preliminary correlations with electrical performance. An attempt was made to design the sputtered MEA for use in a DMFC, and directions for future work are offered. Films have been characterized by X-ray diffraction (XRD), energy dispersive X-ray analysis (EDAX),

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Rutherford backscattering spectroscopy (RBS), and X-ray photoelectron spectroscopy (XPS). By using an ultrathin layer of highly electroactive catalyst prepared by sputter deposition, DMFC operation has been demonstrated with anode catalyst loading levels as low as 0.03 mg/cm² in a cell with a 25 cm² active electrode area. These preliminary studies imply that improvements in the film morphology and MEA processing will offer substantial improvements in power density.

Experimental

The sample MEAs used in this study will be designated PtRuSp_i, *i* being a number increasing with anode catalyst loading. PtRu films were sputtered under two different conditions. Films for MEAs PtRuSp0-2 were sputtered at ~160 V dc and 250 mA in 20 mTorr argon, directly onto both the Nafion 117 membrane and carbon Toray 060 electrode. The target used under these conditions was a 2 in. diam, hot-pressed 52:48 mixture of Pt and Ru metal powders. The substrate was ~15 cm from the target, so metal atoms were expected to be thermalized before deposition. The films for MEA PtRuSp3 were sputtered in a table top sputtering unit at ~1800 V dc and 26 mA in 100 mTorr argon. In the latter case the target was 2-3 cm below the substrate. The second target was a Pt ring that had been electrochemically plated with equiatomic PtRu. The composition of this target became Pt rich as the plated material was sputtered away. For each MEA, the film sputtered on the carbon electrode had deposition conditions (pressure, current, voltage, etc.) identical to those of the film sputtered on the membrane, but there is some difference in membrane and electrode film thickness (sputter time).

A Cambridge S250 scanning electron microscope (SEM) was used to measure nominal film thicknesses of sputtered films. Cross-sectional thickness analyses of the MEAs were performed after DMFC testing by fracturing the MEA; immersing an MEA section in liquid nitrogen for a couple of minutes, and then applying a bend stress resulted in a neat fracture. EDAX was performed using a Kevex Quantum Detector with an IXRF digital pulse processing analyzer to determine the metallic compositions of the films. As-sputtered films were characterized *ex situ* by XRD with an Inel CPS-120 diffractometer (using Co K α radiation, $\lambda = 1.7902$ Å) to determine their phase compositions and approximate chemical compositions. As-sputtered films were examined by RBS using 2 MeV α -particles to determine their thickness and metallic compositions. In all cases, RBS measurements were performed on samples taken from >3.5 cm from the center (maximum thickness) of the deposition region. Finally, a Surface Science Instruments SSX100/05 XPS spectrometer was used with Al K α radiation to test films *ex situ* before and after use in a DMFC to investigate their metallic compositions and the presence of oxides. XPS was performed on one of the films presented here, and results obtained from these measurements are representative of this type of catalyst layer.

MEAs with total anode catalyst loadings of 0.03, 0.1, 0.3, and 1.0 mg/cm² were fabricated. In some cases, a thin coating of Nafion ionomer was sprayed over the PtRu film deposited on the Nafion 117 membrane to make a continuous proton conducting path between the catalyst material and membrane. To prevent cathode polarization and methanol crossover from affecting the results of our tests, cathode catalyst layers with 12 mg/cm² of Pt were applied from catalyst ionomer inks and this was not varied throughout the course of the studies. All subsequent mention of catalyst in this work is assumed to be in reference to PtRu at the fuel cell anode. Subsequent MEA processing continued as reported previously.^{5a} Cells were tested with oxygen at 20 psig and 1 M methanol at 90°C. Anode polarization studies were performed using the cathode as a pseudoreference electrode that sustained the hydrogen evolution reaction.^{5b}

Results and Discussion

Figures 1a and b show SEMs of the catalyst film in MEA PtRuSp2 after use in a DMFC. Figure 1a is a medium magnification shot of a fractured MEA, showing the configuration of its compo-

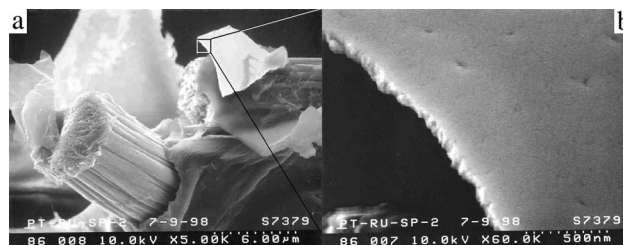


Figure 1. SEMs of MEA PtRuSp2 after use in a DMFC, showing (a) configuration of components (Nafion membrane, catalyst particle, and Toray carbon electrode) in MEA and (b) detail of film microstructure.

Table I. Film parameters for PtRu catalyst layer.

MEA	Atomic composition		Total film thickness (nm)	Loading (mg/cm ²)
	RBS ^a	EDAX ^b		
PtRuSp0	Pt _{0.68} Ru _{0.32}	Pt _{0.39} Ru _{0.61}	14 ^{a,c}	0.03
PtRuSp1	Pt _{0.63} Ru _{0.37}	Pt _{0.37} Ru _{0.63}	44 ^{a,c}	0.1
PtRuSp2	Pt _{0.63} Ru _{0.37}	Pt _{0.31} Ru _{0.69}	140 ^{b,d}	0.3
PtRuSp3	—	Pt _{0.84} Ru _{0.16}	~1000 ^{b,d}	1.0

^a As-sputtered.

^b After DMFC use.

^c RBS (sum of membrane and electrode films).

^d SEM (sum of membrane and electrode films).

nents (carbon electrode, catalyst films, and Nafion) at the catalyst/electrode interface. The films are in large (several micrometers across) plates, the mean plate dimensions changing with film thickness. Figure 1b includes a high magnification detail of the edge of one such catalyst plate. It is flat, and the edge indicates the columnar microstructure expected for zone 1 type deposits.¹⁸ It is clear from the figure that the catalyst particle was broken from a larger film, but it is not certain whether the coherent sputtered film was broken up during hot-pressing, by swelling of the membrane during the uptake of water while it was oxidizing methanol in the DMFC, or during the SEM sample preparation. These micrographs are also representative of the films in MEAs PtRuSp0 and 1. The sputtered films in PtRuSp3 look more like small chunks with a mean dimension of 60-100 nm, a difference which is attributed to the different sputtering conditions. EDAX showed film compositions (included in Table I) to be Ru rich, except for that of PtRuSp3, which was extremely Pt rich. XRD showed the films to be single phase and to have lattice parameters equivalent to that of chemically prepared Pt₁Ru₁. As Pt-Ru alloys are known to follow Vegard's law, the compositions of these films are close to Pt₁Ru₁.²⁶

Figure 2 shows RBS spectra obtained from several as-sputtered catalyst films, used to determine their bulk compositions and thicknesses. The thickness values, included in Table I, are consistent with weight changes measured before and after SD as well as thicknesses determined from SEM. While RBS was used to measure compositions before use in a DMFC, the same technique could not be applied to films after DMFC use. Hence, EDAX was used to characterize films after use. Because a single technique was not used to determine film composition before and after DMFC use, and each method probes a different surface to bulk ratio, we cannot say with certainty whether the difference corresponds to differences in the techniques or to changes resulting from catalyst use. However, because each individual technique shows a variation in composition of only 10-15%, these measurements have determined that the film compositions are fairly consistent. Although some difference in composition values measured by the two techniques is to be expected

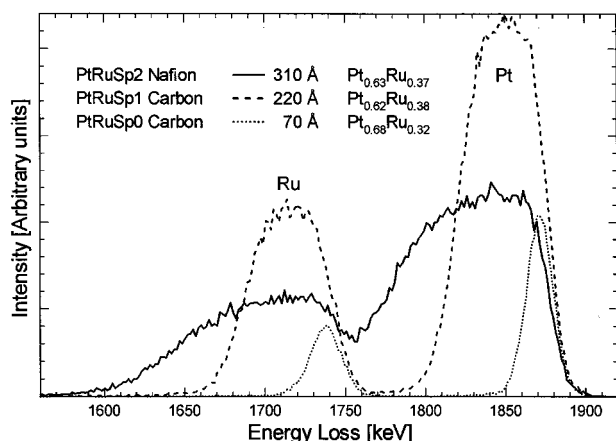


Figure 2. RBS spectra of several sputtered PtRu films.

ed, we do not expect large changes in bulk compositions resulting from DMFC use because Pt and Ru should both be stable in the applied potential ranges.

XPS data for Pt-Ru thin film catalysts as-sputtered (—) and after use in a DMFC (-----, PtRuSp2 and others) are shown in Fig. 3a and b. Figure 3a contains the Pt $4f^{7/2}$ (71 eV) and $4f^{5/2}$ (74.5 eV) peaks. The shoulders at high binding energies (72.5 and 76 eV) represent Pt oxides. In Fig. 3b, the Ru $3d^{5/2}$ (280 eV) and $3d^{3/2}$ (284.1 eV) peaks and their oxides (281.5 and 286 eV) are confused by overlap with peaks from C 1s (284 eV) and its fluoride (291 eV). Analysis by Gaussian deconvolution determined that as-sputtered films contained no Pt oxide and a small amount of Ru oxide. After use in a DMFC, anywhere from 15 to 35% of the surface Pt was oxidized (depending on the sample tested). Although the amount of Ru oxide could not be quantitatively determined because of overlap with the carbon peak at 284 eV, the proportion of Ru metal to Ru oxide is estimated to be the same as that of Pt metal to Pt oxide.

Use in a DMFC increased the amount of Pt and Ru surface oxide present in the anode catalyst. Pourbaix diagrams for bulk Pt and Ru suggest that both metals are in the metallic state at the potentials and pH used in the cell. However, several researchers have found that Pt-O species develop on roughened Pt at potentials far below that at which planar Pt is oxidized.²⁷ The increase in oxide species after DMFC use also suggests that the thin film catalyst layer has roughened, which would increase the electroactive surface area. The film surface composition measured by XPS after use in a DMFC was Pt rich, $Pt_{0.58}Ru_{0.43}$. While the surface composition of this film was not measured by XPS before use in a DMFC, the surface composition of an equivalent PtRu film before use was almost equiatomic

($Pt_{0.52}Ru_{0.48}$). Thus, surface metal atom oxidation and the associated film surface reconstruction could be responsible for this apparent change in surface composition. Further investigation of these changes is in progress, and will be presented in a future publication.

Figure 4 shows E-i characteristics of the cells listed in Table I. Cells were operated at 90°C in 1 M methanol at high flow (0.1-0.5 lpm) with 4 lpm oxygen at 20 psig. The cell performance of MEAs PtRuSp1-3 increases with catalyst loading for the series 0.1, 0.3, 1 mg/cm², represented by closed symbols in the figure. The best performance was attained with MEA PtRuSp3. For this MEA, a cell voltage of 0.4 V was realized at ~135 mA/cm², and the cell gives a voltage of 0.309 V at 300 mA/cm² and 0.167 V at 600 mA/cm². The maximum power density achieved by PtRuSp3, at 1.0 mg/cm² loading, was 104 mW/cm², or about one-third of that of a state-of-the-art DMFC.^{5c}

IR-corrected anode polarization data (not shown here) yields a Tafel slope at low current densities of ~115 mV/dec. This Tafel slope is comparable to that obtained by anode polarization measurements of chemically prepared PtRu powder catalyst.²⁸ Comparing anode polarization values to cell data suggests that cathodic losses are not significant in determining the shape of the cell E-i curve. This is a result of the large cathode catalyst loading (12 mg/cm²) and the relatively low current densities that were used to test the cells.

In an attempt to improve the MEA structure, PtRuSp0 with 0.03 mg/cm² was prepared without spraying Nafion on the membrane after catalyst deposition. It had equivalent amounts of catalyst sputtered on both the electrode and the membrane. As seen in the figure, this MEA (represented by the open symbol in Fig. 4) performed as well as PtRuSp2, which had ~10 times (0.3 mg/cm²) the catalyst, with one-third of this catalyst on the electrode and two-thirds on the membrane. We believe that the catalyst deposited on the membrane in PtRuSp2 has been electrically isolated from the electrode by the Nafion spray. By removing the spray, we have increased the chance that the catalyst on the membrane would be in electrical contact, and it appears that the ion-conduction is readily permitted.

Because PtRuSp0 (with no Nafion spray) reached power densities comparable to those attained by the sputtered MEAs with higher loadings and Nafion spray, we think that the *ex situ* addition of Nafion to the MEA is not necessary to fulfill the requirement for proton conductivity. It is possible that the hot-pressing step in manufacturing the MEA intimately connected the carbon electrode, sputtered PtRu catalyst, and Nafion membrane, providing a proton-conducting path. However, it is desirable to eliminate the hot-pressing step from the MEA processing. Raistrick showed that proton conductivity in H₂-air fuel cell MEAs produced by Nafion impregnation could be accomplished just as well by replacing the Nafion with RuO₂.²⁹ It could be that the RuO₂ detected here by XPS in used MEAs is present as hydrous RuO₂ in the active cell and conducts protons sufficiently well that Nafion is not needed in the MEA catalyst layer. The

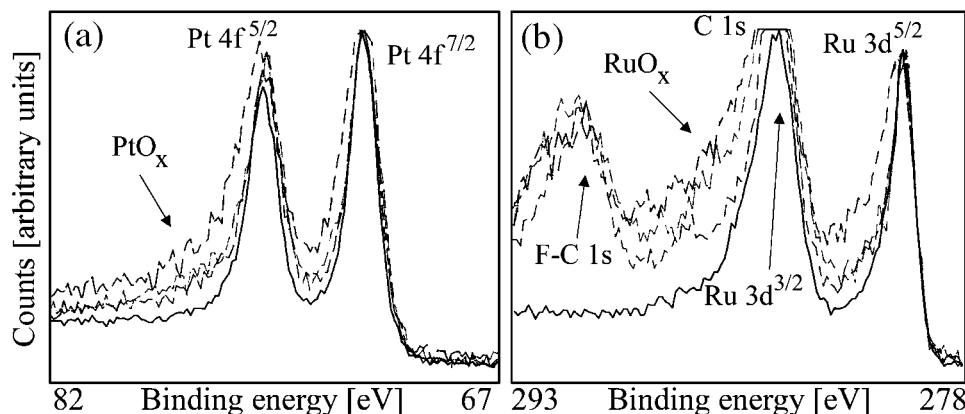


Figure 3. XPS spectra of PtRu thin film as-sputtered and after use in a DMFC. (a) Pt 4f peak and (b) Ru 3d peak.

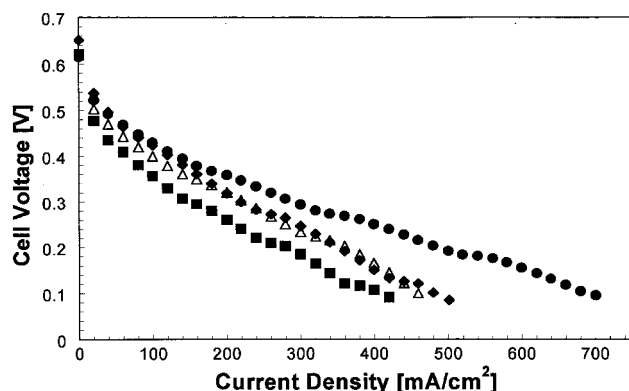


Figure 4. Cell voltage data for DMFCs with sputtered catalyst. Cells run at 90°C with 4 lpm O₂ at 20 psig, and 1 M methanol. PtRu Loadings: ● 1.0 mg/cm², ◆ 0.3 mg/cm², ■ 0.1 mg/cm², △ 0.03 mg/cm².

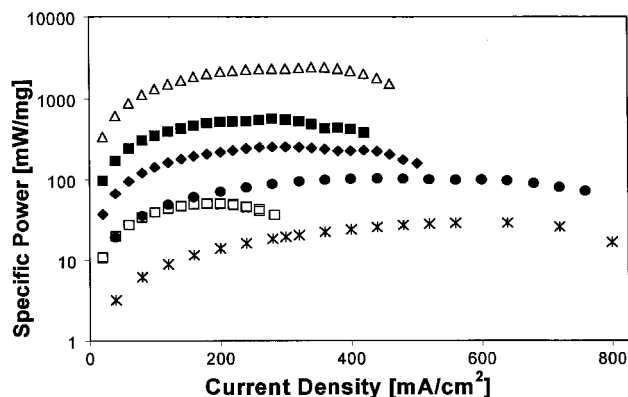


Figure 5. Catalyst utilization curves for sputter deposited, carbon supported (□), and conventional (*) PtRu. Loading in mg/cm² (△ 0.03, ■ 0.1, ◆ 0.3, ● 1, □ 1, * 8).

equivalence of the proton conductivity of Nafion to that of RuO₂ in the MEA catalyst layer was also seen by Gottesfeld *et al.*⁶ This suggests the possibility of exploiting RuO₂ as a proton conductor to replace Nafion in the proton/electron/fuel conducting structure of the MEA.

The effectiveness or utilization of the anode catalyst can be determined by dividing the power output of each cell by the amount of anode catalyst used. This measure of catalyst utilization expressed in milliwatts per milligram is plotted as a function of the current density in Fig. 5. Such a representation focuses on the need to achieve not only a reduced catalyst loading but also the high utilization at practically significant current densities. Included in this graph are specific power curves of conventional unsupported and supported PtRu catalysts. While a conventional unsupported PtRu catalyst gives a specific power output of ~100 mW/mg, this can be increased by over an order of magnitude by SD of the PtRu catalyst. This suggests that a DMFC with a SD anode catalyst can be made with 1/25th the amount of anode catalyst as one with conventionally prepared MEAs.

Conclusions

We have demonstrated the feasibility of a DMFC with sputter-deposited PtRu anode electrocatalyst. By depositing the catalyst in ultrathin layers directly on the Nafion membrane and carbon paper electrode, the utilization of the catalyst has been increased by almost two orders of magnitude. This preliminary study is very encouraging concerning the reduction of the anode catalyst loading below the ~4 mg/cm² used in conventional MEA processing.

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